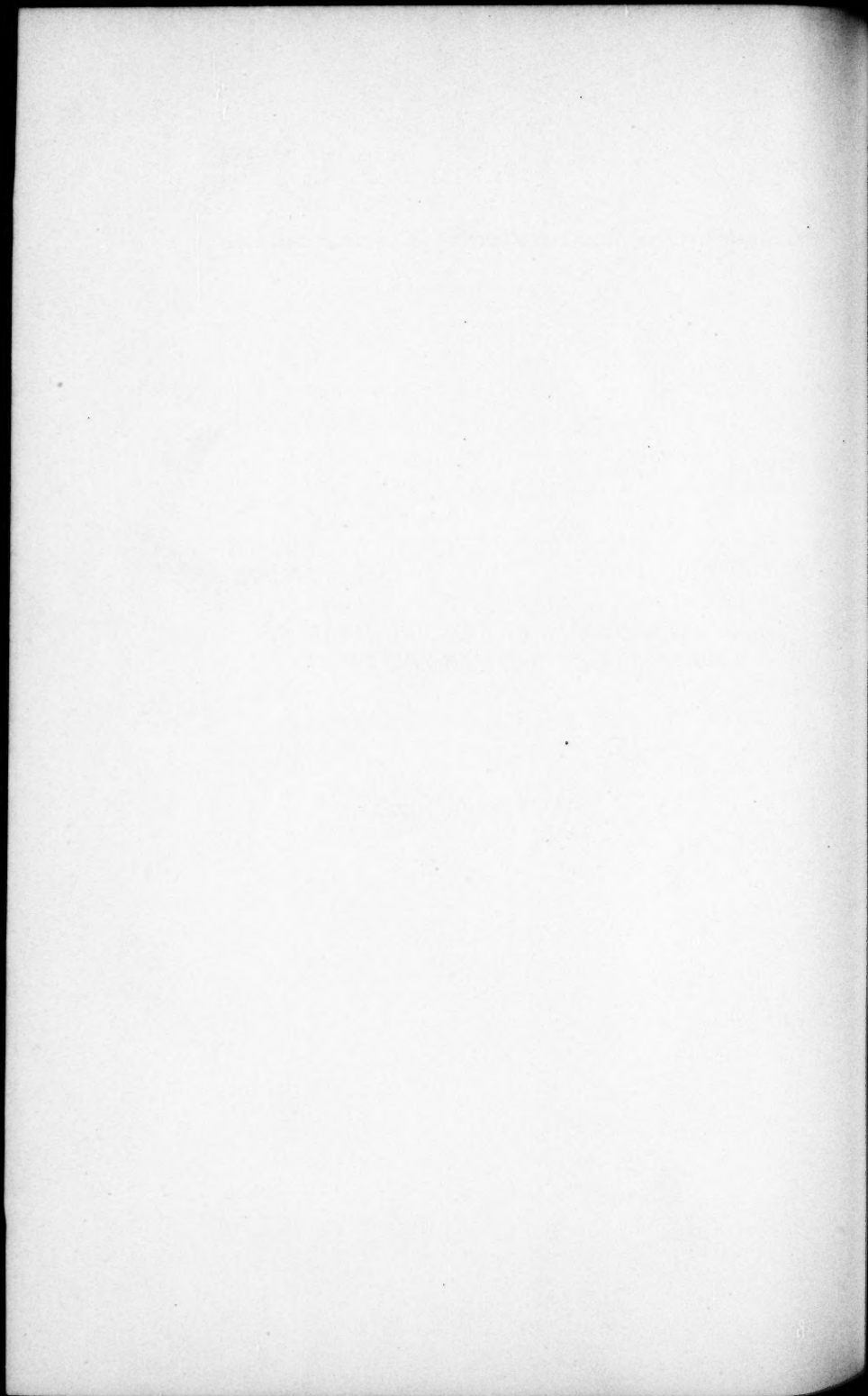AN IMPROVED METHOD FOR DETERMINING SPECIFIC
HEATS OF LIQUIDS, WITH DATA CONCERNING DILUTE
HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, NI-
TRIC AND PERCHLORIC ACIDS AND LITHIUM,
SODIUM AND POTASSIUM HYDROXIDES.

By T. W. Richards and A. W. Rowe.

AN IMPROVED METHOD FOR DETERMINING SPECIFIC HEATS OF LIQUIDS, WITH DATA CONCERNING DILUTE HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, NITRIC AND PERCHLORIC ACIDS AND LITHIUM, SODIUM AND POTASSIUM HYDROXIDES.

By Theodore W. Richards and A. W. Rowe.

In a previous communication [1] the authors described a new and accurate method for the determination of the specific heats of liquids, based upon the adiabatic procedure originally outlined by one of us.[2] Any method for this purpose demands an exact quantitative source of heat; and in the present case the device employed was the liberation in parallel experiments of known amounts of heat by the neutralization of an acid with a base. The neutralization was carried out in the center of a calorimetric system consisting primarily either of water or of the liquid under observation. By observing the relative temperature rise in the system when first water and subsequently the other liquid filled the calorimeter, (or better, by so arranging the parallel experiments as to secure uniform temperature changes in the two cases, comparing the relative weight of liquid used with that of the original amount of water) a direct determination of the relative heat capacities of the two systems was rendered possible. The chief advantage of such methods involving the comparison of one set of data with another is that possible errors of direct determination appear in all experiments and are thus eliminated by cancellation.

As originally outlined, the method had one distinct objection, namely, the alkali was at first contained in a reservoir outside the calorimetric system and at a temperature usually somewhat different from the latter. Although the difference was carefully determined and a suitable correction applied for the heat thus abstracted from or

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[1] Richards and Rowe, Proc. Am. Acad., **43**, 475 (1908); Zeit. phys. Chem. 64, 187 (1908).

[2] Richards, Henderson and Forbes, Proc. Am. Acad., **41**, 3 (1905).

brought into the system, this feature introduced uncertainty, especially as the liquid might undergo slight but undetermined changes in temperature during the act of transference. This point was recognized by the authors at the time of the initial publication and at that time a method for its elimination was suggested. A description of the improved apparatus and some of the results yielded by it are embodied in the present communication.

METHOD AND APPARATUS.

As in the earlier form, the neutralization of sulphuric acid with sodium hydroxide was selected as the source of heat. The stability of solutions made from this acid renders it especially suitable for such purposes. In carrying out the neutralization a concentrated solution of caustic soda was placed in a small stoppered platinum can, which was suspended within a platinum bottle containing the acid to be neutralized. At the appointed moment, the two liquids were allowed to mix. This bottle, closed with a platinum stopper, had previously been submerged in the liquid to be studied, which was itself held in a large platinum calorimeter. The whole was provided with an environment so arranged as to vary in temperature at the same rate as the calorimeter, and this eliminated the troublesome and inexact cooling correction.

It is perhaps worth while to describe the affair in detail because much time was spent in working out the most advantageous arrangement. The accompanying diagram will assist in the explanation. (Figure 1.)

The platinum bottle (D) used to contain the weighed amount of acid was provided with a very wide mouth, in order that the receptacle for the alkali could be introduced within it. The mouth was narrowed by a hollow platinum stopper or cap (E) of peculiar shape, the joint being made tight by a thin smooth rubber band or collar between the stopper and bottle. The upper end of the open stopper was fastened by stout platinum wires to a hollow tube of hard rubber which passed through an opening in the jacket above, and held the bottle in suspension.

The receptacle for the alkali also was unusual in its form, consisting of a very small platinum can (F) (of a diameter slightly less than that of the mouth of the bottle) with a hole in the bottom closed by a small rubber stopper (r). This can was open at the top and was sus-
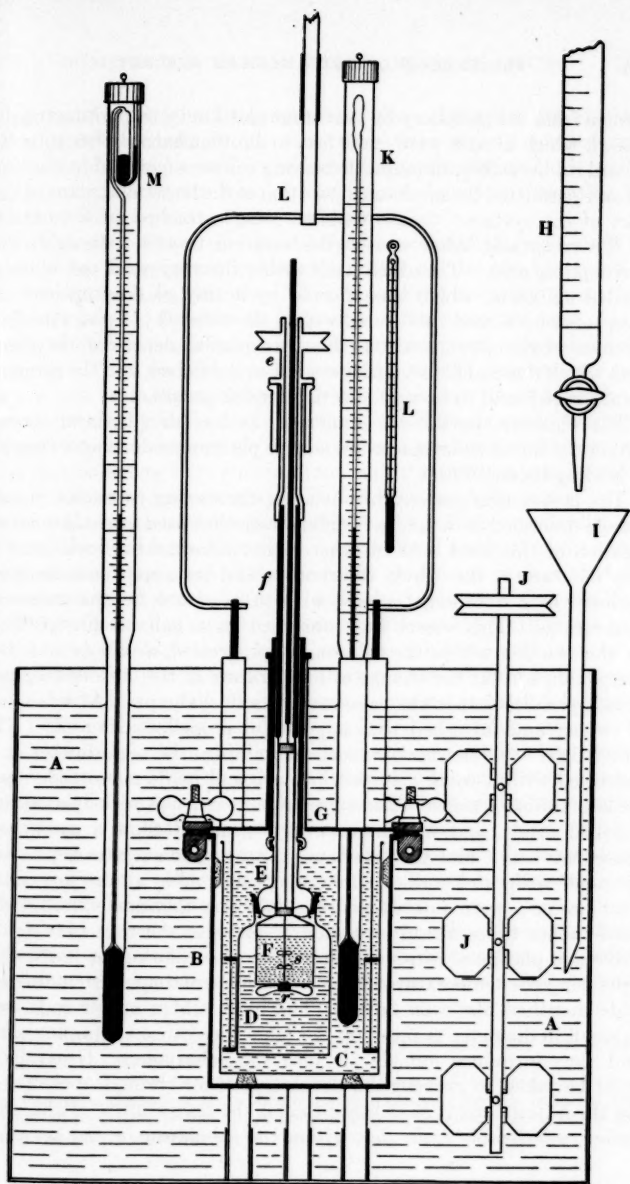
FIGURE 1.

pended from the periphery by four stout platinum wires symmetrically placed, which in turn were made fast to another hard rubber tube (f). A hard rubber pulley and suitable bearing (e) were fastened to the tube (f) and permitted the mechanical rotation in the horizontal plane of this part of the system.   Small platinum wings attached to the outside of the receptacle below caused the rotation to stir thoroughly the surrounding acid.   The alkali itself within the very small can likewise needed agitation, which was effected by a tiny platinum stirrer (s) suspended by a hard rubber rod within the tube (f).   Upon the effectiveness of the stirring within these receptacles depended the speed with which thermal homogeneity could be established, and the arrangements were found to be very effective for this purpose.

The platinum bottle was immersed, as has already been stated, within the liquid to be studied in a large platinum calorimeter capable of holding about 0.7 liter.

The jacket arrangement for obviating the cooling correction should also be described in detail, as it differs from that used in the last investigation of this kind.   As in other recent calorimetric work done in this laboratory, the whole calorimeter and its appurtenances were enclosed in a water-tight vessel, with tubes above for the necessary connections.   This vessel was immersed in a pail of dilute alkali. As the reaction within the calorimeter progressed, acid was added to this alkali, so that the change of temperature in the surrounding pail should parallel that in the calorimeter itself.   The pail (A) was made of copper and furnished with a powerful propeller-stirrer (J).   The water-tight "submarine" vessel containing the calorimeter was furnished with a cover clamped in place and made water-tight by a smooth rubber washer.   The submarine vessel was nickelplated and polished inside, and was large enough so as to allow a narrow air space between it and the calorimeter, from which it was kept apart by small wedges of cork.   Through suitable tubes at the top of the "submarine" were introduced not only the thermometer and the hard rubber tubes already mentioned, but also the rods bearing the two-stage platinum stirrer which stirred the calorimeter itself, thus equalizing the temperature in the liquid immediately surrounding the wide mouthed platinum bottle.   The hard rubber stirrer rods were as small in diameter as possible; for large rods cause a pumping effect and thus introduce outside air into the calorimeter.   Great pains must be taken to prevent the circulation of air through these tubes, for the adjustment is so delicate that if the temperature of the room varies considerably from that within the submarine, a distinct effect

is produced upon the temperature of the calorimeter by air thus introduced. Accordingly all the tubes were loosely packed with cotton wool which served to prevent undue circulation.[3]   A further safeguard against error from this cause was found in increasing the depth of submergence of the "submarine."

Two similar accurately standardized thermometers were used to register the temperature in the calorimeter on the one hand and in the outside bath on the other. For the sake of accuracy these thermometers should be alike in scale and in thermometric lag. Those employed were especially made, and were very well adapted for the purpose. They covered a range from 15.4 to 20.8 degrees, and each degree was 74 millimeters long. A small auxiliary thermometer (L) suspended wholly in the air beside the stems of the larger instruments gave the mean temperature of the exposed portions of these stems. The thermometers were standardized with the greatest care by reference to standard instruments which had been carefully studied at the Bureau Internationale des Poids et Mésures. Their standardization will be described in another place. As the final results usually varied no more from the mean value than 0.05 precent, it is clear that the thermometers were usually to be depended upon to within 0.001°.

In the outer pail of course the concentration of the alkali might vary within wide limits without harm, and the sulphuric acid introduced into it was always the most concentrated grade of pure acid of commerce,[4] which was delivered through a burette graduated in tenths of a degree Centigrade, as already explained in previous papers.

Within the platinum bottle, however, the acid needed very precise determination in order that the heat yielded to the calorimetric system by its neutralization by a slight excess of alkali might be definitely apportioned in each experiment.

The steps taken to prepare these solutions of definite strength are described below. Other experimental details will be discussed later when the individual experiments are described.

With this apparatus, then, were made many series of experiments in which first pure water was contained in the calorimeter-can, and afterwards the various dilute solutions. In each case a definite amount

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[3] The sketch is not strictly drawn to scale and the size of the rods is exaggerated for the sake of clearness.

[4] Crude acid would have answered, but the pure acid was found to be more constant in composition than cheaper cruder grades. As the burettes were graduated to deliver a constant volume of acid for a definite temperature rise, this point was of importance.

of heat was evolved in the inner vessel by means of known amounts of acid and alkali, and in each case the rise in temperature caused by this added heat was duly read off on the thermometers.   Thus with the appropriate calculation, to be described later under the individual experiments, the specific heats of the various solutions were determined.

PREPARATION OF MATERIALS.

The preparation of the materials needed in the experiment naturally divides itself into two categories; first, the preparation of the acid and alkali needed to evolve measured quantities of heat, and secondly, the preparation of the pure solutions whose specific heats were to be determined.   The former of these two categories was a very simple matter and may be described in a few words.

The standard sulphuric acid to be weighed into the bottle within the calorimeter and there neutralized, was prepared twelve liters at a time from the purest obtainable acid and distilled water — the resulting solution being thoroughly shaken to insure complete homogeneity. The concentration was determined by titration against a carefully standardized solution of sodium hydroxide, and finally the liquid was sealed by means of paraffin in two-liter Jena flasks.   The results of the experiments made with this acid solution give abundant testimony as to its permanence and constant content of ionized hydrogen.   That the acid should undergo no change during use, the device described in the earlier article (l. c.) was utilized.   The determinations of the strength of Lot A gave as a mean of the individual titrations the value 6.274 percent.   This was subsequently verified by a series of gravimetric analyses, the mean of which was 6.276 percent.

The much more concentrated alkaline solution for the innermost vessel was made up in the manner previously employed, from Kahlbaum's sodium hydroxide, purified by alcohol.   This solution was protected from further contamination by carbonate through the use of a double attachment; all entering air must pass first through a tower of soda lime, and further through a wash bottle which contained some of the solution from the container, to prevent evaporation of the standard solution into the tower.   (Figure 2)   An excess of the alkali was always taken in each thermal experiment, sufficient to render inoperative the carbonate originally present.   A series of titrations with a carefully standardized hydrochloric acid solution indicated a total alkalinity corresponding to the concentration 27.825 percent of
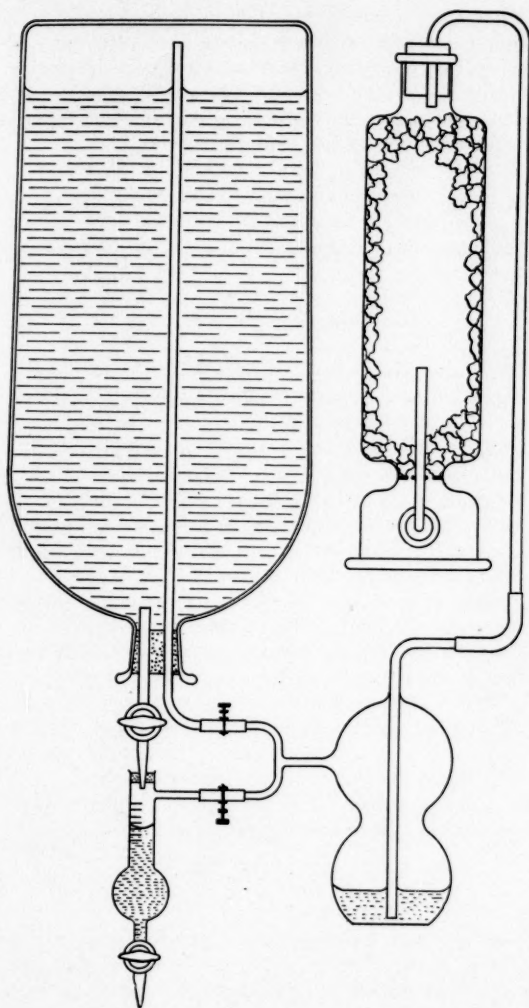
FIGURE 2.

sodium hydroxide — or, expressed in *mols*, NaOH . 5.760 H$_2$O. The sodium present as carbonate — determined by successive titrations using methyl orange and phenol phthaleïn as indicators,—was 1.2 percent of the sodium present. The standardization of the acid and alkaline solutions used for the titrations was based upon a series of gravimetric analyses of silver chloride.

The substances studied in dilute solution were hydrochloric, hydrobromic, hydriodic, nitric, and perchloric acids, and lithium, sodium, and potassium hydroxides, as indicated by the title. The preparation of these substances will be described in order in the pages immediately following.

Hydrochloric acid.

The acid for this solution was obtained by fractional distillation and condensing in quartz the constant boiling mixture of the purest obtainable acid. The middle third of the middle third was selected from two successive distillations and this sample, one-ninth of the material at first employed, was diluted with freshly distilled water to the desired concentration. Two samples were prepared, the first, sample A, being standardized gravimetrically by the precipitation of silver chloride, taking precautions such as one would use in determining atomic weights, and the second, sample B, being estimated volumetrically by titration with very exact standard alkali, standardized by means of the first. The results of these analyses were as follows: 68.3590 and 69.4105 grams yielded respectively 5.3234 and 5.4048 grams of silver chloride. Using the usual atomic weight Ag = 107.88, this acid is thus shown to contain 100.15 gram-molecules of water to one of acid, the two experiments deviating from the mean by only 0.004 percent. The other acid B was found volumetrically to be slightly more concentrated, having 99.97 gram molecules of water. These are so nearly alike that careful determination of their specific heats showed no essential difference between them.

Hydrobromic acid.

The very pure acid used for these experiments was prepared some time ago for determinations of atomic weights. For the present purpose it was redistilled, using a quartz condenser; the first and last portions of the distillate were rejected. The middle fraction used was perfectly colorless. The two portions (over 62 and 70 grams respec-

tively) were carefully weighed in a weighing burette and titrated with standard alkali contained in another weighing burette, the two analyses giving exactly the same result, a percentage of 4.293 grams of hydrobromic acid, which corresponds to a molecular concentration of 100.5 molecules of water for each molecule of hydrobromic acid. This solution, like all the acid solutions, was immediately placed in a large bottle of resistant glass ("nonsol") and the specific heat was determined as rapidly as possible.   It was found that neither this glass nor Jena reagent glass was essentially attacked by the dilute acids during the times in which they were kept therein.

Hydriodic acid.

The preparation of this acid in a state of purity offered considerable difficulty.   Three different samples of the purest commercial product which was guaranteed to conform to the usual analytical standard were purchased, but each contained appreciable amounts of free iodine from which it could not easily be purified.

It should be noted, however, that a small amount of iodine would not have a very important effect on the specific heat, although it was exceedingly important that this amount should not increase during the experiment, because such an increase would superpose the heat of oxidation of the acid upon the phenomena concerned with specific heat.   Therefore careful analyses with sodium thiosulphate were made before and afterwards in order to make sure that, during the determination of the specific heat, no significant oxidation had occurred.   This was the case when the dilution of the concentrated acid was effected by adding water which had been freshly distilled and cooled in an atmosphere of hydrogen, the resulting solution being kept under such an atmosphere protected from oxygen.   During the actual measurement of the specific heat it was not convenient to exclude air, but analysis showed that the decomposition which took place during that brief time was wholly negligible.

Each of the three samples of dilute acid was analyzed as before. The first was found to contain 6.635 percent of hydrogen iodide and 0.032 percent of iodine.   The percentages in the second were 6.625 and 0.031 respectively.   After four experiments on the specific heat another portion of this sample was analyzed and found to contain 6.632 percent of hydrogen iodide and 0.034 percent of iodine, having been essentially unchanged.   The third specimen by acidimetric analysis was found to contain 6.626 percent of acid and 0.040 percent

of iodine.   With these three specimens of acid six determinations of the specific heat were made.   They were all essentially of the same strength and the differences between the specific heats of the different samples did not exceed the error of experiment, the determination of sample A giving a value of 0.9210, three of sample B giving 0.9215 and two of sample C yielding 0.9211 as the respective values of the specific heat.

Nitric Acid.

This solution was prepared from the best obtainable nitric acid through fractional distillation, using a quartz condenser.   To avoid the action of sunlight in forming oxides of nitrogen the operation was performed in a carefully darkened hood.   The middle third of the middle third was reserved.   This was diluted to the proper strength with freshly distilled water.   The concentrated acid was not absolutely colorless, but the exceedingly pale tinge of yellow could not have indicated an amount of lower oxides large enough to affect the determinations of the specific heat of its dilute solution.   The solution was analyzed by titration and properly diluted.

Perchloric Acid.

A solution of this substance was made from a sample of acid of pure material prepared for the determination of the atomic weight of silver and lithium by Dr. H. H. Willard.   The authors take pleasure in expressing their thanks for this courtesy.   The preparation is described elsewhere.[5]   The concentrated acid was diluted to the proper strength with freshly distilled water.   Two analyses each showed the presence of 5.788 percent of perchloric acid which corresponds to a concentration of $HClO_4.99.99 H_2O$.

Sodium Hydroxide.

The preparation and maintenance of the alkaline solutions in a condition free from carbonate offers well known difficulties.   The purest sodium hydroxide of commerce contains appreciable amounts of this impurity; and the contamination is not diminished by the usual methods of handling.   The frequency with which this fact is overlooked will be discussed in another place.   The available data

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[5] Richards and Willard, Journ. Am. Chem. Soc., **32**, 4 (1910).

concerning the heat capacities of carbonate solutions suggest however that the amounts of carbonate to be found in hydroxides of the highest grade would have a scarcely appreciable effect upon the specific heat. For example, the specific heat of a solution of sodium hydroxide with 100 mols of water as determined by Thomsen is 0.968 while that of sodium carbonate of an equivalent concentration is given severally by Thomsen as 0.958 and by Marignac [6] as 0.9695. Taking Thomsen's two values as the more strictly comparable, it is evident that each percent of carbonate may be supposed to lower the specific heat, by one unit in the fourth decimal place. The highest grade of sodium hydroxide to be found in commerce, as employed in our experiments, contained from 1 percent to 2 percent of carbonate; hence solutions made directly from this material would show a heat capacity 0.01 percent to 0.02 percent lower than a solution of pure hydroxide. Because, however, such assumptions introduce uncertainty; and furthermore, because 0.02 percent is a perceptible quantity, it was obviously best to secure specimens of really pure substances.

Our material was prepared by first adding to a rather concentrated solution of the purest material of commerce an excess of pure barium hydroxide in hot aqueous solution. After the settling of the precipitated barium carbonate, the clear, supernatant liquid was siphoned off in an atmosphere free from carbon dioxide. A series of gravimetric determinations of the excess of barium present in the solution were then made, and the theoretical amount of very pure sulphuric acid was added. After the settling of the precipitate, the supernatant liquid was again siphoned off with the usual precautions, and made up to the proper strength by the addition of freshly distilled water, which had been cooled in an atmosphere free from carbon dioxide. Such alkaline solutions were always kept in paraffin-lined bottles — a procedure which sufficiently preserved their initial purity, as is evidenced in the accompanying analyses.

For example, 101.20 grams of solution were found by titration to be equivalent to 9.8976 grams of a certain solution of hydrochloric acid. On the other hand, 12.9746 grams of this latter solution were found to yield 10.3197 grams of silver chloride. Hence, 100.000 grams of the alkaline solution must be equivalent to 7.8723 grams of silver chloride or must contain 2.171 grams of dry sodium hydroxide. The solution contained therefore 2.171 percent of alkali. Other analyses are tabulated below.

The end point was essentially the same with methyl orange as with

[6] Marignac, Arch. Sci. Nat., **55**, 113 (1876).

phenol phthalein, thus showing that the carbonate had been satis-
factorily eliminated.   No barium could be found by careful qualitative
testing in a solution, but a minute trace of sulphate was found there.
This impurity was quite too small in amount to have any effect on the
specific heat.

THE CONCENTRATIONS OF THE PUREST SODIUM HYDROXIDE SOLUTIONS

No.	Date	NaOH(%)	Mols.H_2O
1	April, 1909	2.1710	100.06
2	" "	2.1703	100.10
3	May "	2.1709	100.07
			100.08
4	October, 1909	2.1685	100.18

A solution containing enough carbonic acid to combine with 1.3
percent of the alkali present was also made and standardized in the
same way, the amount of carbonate present being calculated from the
difference between the end points found with the two indicators in
the usual way.   The specific heat of this solution also was taken in a
few experiments.   They did not, however, deviate more from those
with the pure solution than the possible error of the experimentation,
and need not therefore be recorded.   Their evidence at any rate was
enough to verify the prediction made above that the presence of a
small amount of carbonate would have had an almost if not quite
negligible effect.

Potassium Hydroxide.

In the case of potassium hydroxide a similar method was used.
Two samples were prepared, one made up directly from the purest
obtainable commercial product and containing 1.8 percent of its alkali
combined with carbonate, and the other freed from this carbonate in
precisely the manner described in the case of sodium.   The analyses
of these solutions are recorded below.   They were essentially identical
in total alkalinity and no difference whatever could be detected in
their specific heat.   This again supports the conclusion reached in
the case of contamination with sodium carbonate.   The object of
preparing the two solutions in the case of potassium as well as that of

sodium lay not merely in showing the small effect of carbonate, but also in verifying the analytical portion of the work. The agreement of the two solutions showed that no numerical mistake had been made in preparing the solutions, and therefore gave much greater reason for confidence in the accuracy of the final results.

Of the two solutions of potassium hydroxide, the purer was found in two experiments to contain 3.016 and 3.019 percent of the solid substance, and the second less pure solution was found in two other experiments to be equivalent to one containing 3.015 and 3.016 percent of pure substance. The average corresponds to the molecular concentration $KOH.100.1H_2O$. As usual, weights of solution varying from 93 to 132 grams were taken from the weighing burettes in each analysis, hence great accuracy was easily attained.

Lithium hydroxide.

This substance was less easy to prepare, because the material to be had in commerce is very far from satisfactory, as a rule. The substance used in our experiments was of a very high degree of purity, having been made from lithium chloride almost pure enough for the determination of atomic weights. The chloride had been prepared in the first place by Dr. H. H. Willard as one of the preliminary stages of an investigation carried out by him in collaboration with one of us upon the atomic weight of this metal, and its purification has been described elsewhere. We are greatly obliged to him for this help. The salt contained entirely negligible amounts of other bases. After two recrystallizations carried out in order to be sure that no other anions were present, the chloride was converted into the sulphate by heating in a platinum dish with a small excess of very pure sulphuric acid. The pure white salt thus obtained was dissolved in water and the fairly concentrated solution was treated with an excess of hot aqueous barium hydroxide. After settling, the solution was filtered and the excess of barium, determined gravimetrically, was precipitated by precisely the proper quantity of lithium sulphate. The clear solution obtained after settling was decanted in an atmosphere free from carbon dioxide; and after its concentration had been determined, the solution was diluted with enough water, also free from carbon dioxide, to attain the desired concentration. Thus the latter part of the procedure was essentially like that employed in the case of the other alkalies, and the product was strictly comparable with those used in the other cases. In this solution no trace of barium or carbon dioxide

were found upon careful qualitative analysis, but here as in the other cases a trace of sulphuric acid was detected. Two analyses gave identical results, showing that the solution contained 1.307 percent of solid hydroxide, thus possessing the concentration LiOH, $100.4H_2O$.

It will be noted that in some cases, particularly in the case of lithium, the solution was not exactly of the concentration MX 100 H_2O. A moment's consideration will show, however, that the specific heat of such a solution is different by only a negligible amount from one of the exact strength. For example, the specific heat of NaOH 100 H_2O is 0.9664 and that of NaOH 200 H_2O is 0.9827. Evidently then the addition of a single H_2O to the 100 H_2O already present will make a difference of less than 2 in the fourth decimal place, and 0.4 H_2O will cause a difference of less than 1 in that place,— an amount beyond the range of accuracy of the experiments.

In making the calculations the following international atomic weights have been assumed O = 16.000, H = 1.008, Cl = 35.458, Br = 79.916, I = 126.99, N = 14.008, K = 39.09, Na = 23.00, Ag = 107.88.

THE EXECUTION OF THE DETERMINATIONS.

Having thus discussed briefly the details of the apparatus and of the purification of the substances employed we may turn to the execution of an experiment. In order to follow the description reference to the figure on page 175 is necessary.

The "submarine" vessel was first secured in position with its lid off, the outer bath was filled almost to the rim of the vessel, and the temperature of its crude dilute alkali was brought to the point at which the determination was to start. The liquid whose specific heat was to be determined was then placed in the platinum calorimeter, brought to the desired temperature, rapidly weighed to the nearest centigram, and placed in position within the "submarine."

The cover of the "submarine," temporarily suspended from a stand in the neighborhood of the calorimeter, had been already fitted with its various attachments, ready to be clamped into place. First, the open cap (E) of the platinum bottle had been arranged in such a way that the rest of the apparatus could be attached below it. Then the receptacle for the alkali, (F) made water-tight by means of a rubber stopper (r) placed in the hole in the lower part, was fixed in place. After the calorimeter had been prepared as described above, the required portion of caustic soda solution was measured into its recep-

tacle (F) through a burette, and the piece was suspended from its proper place in the lid of the submarine vessel below the cap (E). Extremely accurate determination of the amount of alkali was not necessary, for its concentration was such that its own heat of dilution was approximately that required to raise itself through the temperature range of an experiment. Any excess therefore was self-heating and made no appreciable effect on the rise of temperature caused by neutralization; but nevertheless careful measurement with a burette insured the use of very nearly the same quantity in each case. There was always the same slight excess over and above the amount needed to neutralize the acid.

The standard acid, the one reagent whose quantity needed accurate determination, was next weighed into the wide mouthed platinum bottle (D). It was then rapidly brought to the desired temperature and made fast by a water tight rubber collar to its open cap (E), which had been previously suspended beneath from the cover of the submarine vessel above the receptacle for the alkali, as already stated. The calorimeter-stirrer was then added through its proper holes in the lid, and the whole system attached to this lid (or cover) was transferred to the submarine vessel, the bottle being immersed in the calorimeter. After the screws had secured the lid in place and made it water-tight with the help of the large rubber washer, the level of the outer bath was raised by adding dilute caustic soda, and the various stirrers were set in motion. A very few minutes sufficed to establish thermal homogeneity. The addition of a little ice-water or acid permitted the ready regulation of the bath temperature. When the temperature of the system had become uniform, the inner thermometer was carefully read and the result was recorded as the initial temperature of the experiment. The calorimeter-stirrer, operating at a rate of 45 strokes per minute was found to produce practically no mechanical heat in the time of the experiment, and the effect of outside air which might be pumped in through the openings was also found to be negligible during this time, unless the temperature of the room was widely divergent. Hence no corrections had to be applied for these otherwise disturbing side-effects.

All being ready, the rubber stopper was forced out of the receptacle containing the alkali, and the concentrated caustic soda solution was allowed to flow into the standard acid. At the expiration of three minutes the receptacle, still rotating, was lowered almost to the bottom of the bottle, thus permitting a free mixing of the acid and alkali, which was hastened by raising and lowering the receptacle at appropriate

intervals.   The complete neutralization within the platinum bottle was
abundantly proved by the constancy of the readings of the thermom-
eter after six or eight minutes.

This reaction within the platinum bottle furnished heat which
raised the outer liquid under investigation about four degrees in
temperature.   Because the source of heat was completely surrounded
by the calorimetric liquid, which in turn was adequately stirred,
irregularity of heating effects during the mixing of the acid and alkali
could not be attended by any thermal loss.   From the curve showing
the rise of temperature with time (Figure 3), it is clear that 95 percent
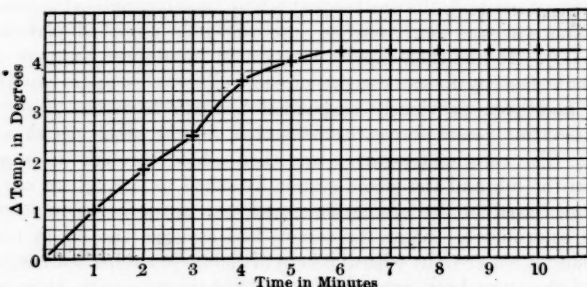

Figure 3.   Temperatures in degrees and time in minutes are plotted as
ordinates and abscissae respectively.   At the expiration of three minutes the
inner stirring was greatly increased by the raising and lowering of the inner-
most vessel.

of the rise occurs during the first five minutes.   This somewhat
rapid rise was easily paralleled in the outer vessel by adding acid so
that there was no difficulty in making the calorimetric operation
fully adiabatic.

The total heat capacity of the apparatus was equivalent at first
to 12.24 grams of water, made up as follows: 252.22 grams of plati-
num constituting the calorimeter, stirrer, bottle, cap and suspension,
together with the small alkali container within the bottle, was assumed
to have the specific heat 0.0324, a value taken as the most probable
after comparing a large number of recent determinations.   This
platinum contained a little iridium, but not enough to affect seriously
its specific heat.   The 3.3 grams of rubber had a water equivalent
equal to 1.59.[7]   Later a heavier rubber stopper was used, increasing

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7 Haldane, Gee and Terry, Report, Brit. Ass., **59**, 516 (1889).

the water equivalent of the rubber to 2.02.   The thermometer had a
bulb occupying 3.90 cubic centimeters.   Taking its heat capacity per
cubic centimeter according to Ostwald-Luther's well known experience,
this corresponds to a water equivalent of 1.83.   The immersed stem
above the bulb was estimated to have a heat capacity of 0.65 on the
same basis, by careful weighing of bits of glass tube of the same
diameter and thickness.   The sum of all these water equivalents was,
as has already been stated, 12.24.   About 114.8 grams of dilute
sulphuric acid (requiring 21.37 grams of the concentrated caustic
soda) were used for neutralization.   The specific heats of these two
solutions were taken respectively as 0.950[8] and 0.8345.[9]   The uni-
formly employed excess of caustic soda (about 3 percent) above the
amount needed to neutralize exactly the sulphuric acid could be neg-
lected because its heating effect was enough to raise it through the
same range of temperature as the main experiment in the way already
explained.   Hence the water equivalent of the sulphuric acid was 109.1
and of the caustic alkali 17.83.   It will readily be seen that the specific
heat of neither sulphuric acid nor caustic soda needed to be known
with very great accuracy because they were essentially constant in
all the experiments.   A slight error therefore would have a wholly
negligible effect on the results, which are relative in their character.
For example an error of 2 percent in the value assumed for the spe-
cific heat of the acid could only affect the final results by a few thou-
sandths of one percent, and there is no likelihood that the assumed
specific heat was anything like so much as even one percent in error.

DATA OF A SPECIMEN EXPERIMENT UPON PURE WATER.   SER. IA,

No. 1.

Temperature Data.

Initial Thermometer reading	$=$	$16.524°$
Total Calibration Correction	$= -$	$0.033°$
Initial Temperature (corrected) (T_1)		$= 16.491°$
Final Thermometer reading	$=$	$20.752°$
Total Calibration correction	$= -$	$0.038°$
Final Temperature (corrected) (T_2)		$= 20.714°$
Temperature Interval $(T_2-T_1) =$		$4.223°$
Stem Exposure Correction	$= +$	0.001
T_2-T_1 corrected		$4.224°$

[8] Marignac, Arch. sci. nat., **2**, 39, 217 (1870); Cattaneo, Cim., **3**, 26, 50
(1889). Thomsen, Ther. Untersuch.
[9] Determined by the Authors. The experimental data will be given in
another paper.

Heat Capacity Data (in terms of water equivalent).

Water in calorimeter	= 450.19 grams	
Calorimeter and fittings	= 12.24	"
21.37 gms. NaOH (sp. ht.= 0.8345)	= 17.83	"
114.80 gms. H$_2$SO$_4$ (sp. ht.= 0.95)	= 109.06	"

Total Heat Capacity	= 589.32	"
Total evolution of heat (Q) 589.32×4.224°	2489.3 calories	
Heat per 100 grams of acid (Q_{100})	2168.4	"
Heat per ½ Mol Acid (U)	16949	"

For the sake of convenience, the heat evolved per gram equivalent of sulphuric acid is called U.

All the other experiments upon water were essentially similar in character to this. They were, however, carried out at several different temperatures in order that the temperature coefficient of the reaction might be measured under precisely the conditions of the experiment, because the heat of neutralization varies decidedly with the temperature. The final temperature of the reaction is taken as the temperature corresponding to isothermal evolution of heat, because the heat capacities of the factors were used in computing the total heat capacity.[10] In this and in all the subsequent computations the specific heat of water over the same range is taken as the unit. As the matter is entirely one of comparison between similar experiments, this is entirely permissible and reduces all to the same basis. After these introductory remarks the two series of experiments with water alone in the calorimeter at about 20.7° and 19.8° C. are given below in order that the range of accuracy of the experiments may be seen. In this table, as before, Q_{100} stands for the heat evolved during the neutralization of 100.0 grams of dilute acid, and U signifies this same result calculated in terms of the gram equivalent of sulphuric acid.

Inspection of the results shows on the whole a very satisfactory constancy. The three experiments of Series I deviate from the mean by less than one-fortieth of one percent, all having been taken at about the same temperature. The five experiments of the next series are less satisfactory, but the last three are completely concordant with one another and with the mean.

From the two averages 16,946 and 16,993, taken at 20.72° and 19.77° respectively, it is easy to compute that the temperature co-

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10 Richards. Journ. Am. Chem. Soc., **25,** 209 (1903).

TABLE II.

WATER STANDARDIZATION.   SERIES I AND II.

No.	Acid Sample.	Water.	Acid.	T_2.	$T_2 - T_1$.	Q_{100}.	U
		gms.	gms.			calories.	calories.
1	Aα	450.19	114.80	20.72°	4.224	2168.4	16949
2	"	450.18	114.86	20.70	4.224	2167.4	16942
3	"	450.16	114.88	20.74	4.226	2168.1	16947
Total av'ge		450.18	114.85	20.72	4.2247°	2168.0	16946
1	Aα	450.18	114.86	19.72°	4.235°	2173.0	16986
2	Aα	450.17	114.85	19.82	4.237	2175.8	17008 *
3	Aβ	450.15	114.85	19.75	4.233	2173.7	16991 *
4	Aβ	450.17	114.86	19.79	4.233	2173.5	16990 *
5	Aβ	450.18	114.86	19.77	4.233	2178.5	16990 *
Tot'l av'ge		450.17	114.856	19.77	4.2342°	2173.9	16993

* The new and heavier rubber stopper increased the water equivalent by 0.43 grams.

efficient of the reaction $\dfrac{\Delta U}{\Delta T}$ under these circumstances is –49.5 calories.

From time to time, in order to show that the acid was remaining constant in composition and that each of the two-liter flasks used for the storage of the acid contained material of the same concentration, the experiments were repeated at other temperatures. With the help of the temperature coefficient just calculated, one finds that at 20°.00 the reaction should evolve 16,982 calories, at 20.47°, 16,957 calories, and so on. It was thus possible to compare the observed evolution of heat at different temperatures with that calculated in this way, and thus use these determinations as a check on the concentration of the sulphuric acid,— or, viewed from the other standpoint, as a means of testing the accuracy of the temperature coefficient. The experiments thus made from time to time are given in the following table.

Incidentally it may be noted that Greek letters are used to designate the several two-liter flasks containing different portions of the same acid.

TABLE III.

CHECK DETERMINATIONS WITH WATER.

No.	Acid Sample.	Water.	Acid.	T_2.	$T_2 - T_1$.	U (obs.).	U (calc.).	At Diff. (calories).
		gms.	gms.					
1	Aβ	450.18	114.87	20.47°	4.225°	16957	16958	−1
2	Aγ	450.17	114.85	19.95	4.232	16988+	16985	+3
3	Aϵ	450.19	114.87	20.68	4.222	16946	16947	−1
4	Aζ	450.19	114.87	20.47	4.227	16963+	16958	+5
Total av'ge		450.18	114.865	20.39	4.227			

The agreement of these results is highly satisfactory, two of them giving essentially the calculated values and two others deviating by an amount corresponding to only about 0.001°, the probable error of experimentation. The last experiment was made with the last portion of the original 12 liters of acid, nearly four months having intervened since the first experiment.

The results recorded in these tables warrant the assumption that the acid furnishes a definite quantitative source of heat, which may be depended upon; and also that the method of evolving and measuring this heat has now been brought to within a range of accuracy as great as is needful under the circumstances.

Having thus prepared the way, we may now proceed to describe the work with the various solutions under consideration.

From the above determinations, it was possible to compute the exact amount of heat which would be liberated by the neutralization of a given portion of acid within the temperature limits of the standardization. By replacing the water of these earlier experiments by a definite amount of some other liquid, a direct determination of the specific heat of the latter could be made. As has already been stated, the experiments were so conducted — by regulating the amounts of liquid used — that the temperature rise in all the determinations was substantially the same. The case of HCl 100 H_2O may be taken as

, typical.   After it has been described in detail, the other cases will be given in tabular form.   The purification of the acid and the preparation of the solution of the proper strength was already been described.

Although the method was similar to that employed in the case of the water, it will perhaps be best to give the details of a single experiment, before all the data are given in tabular form.

In the case of the hydrochloric acid and in all the subsequent cases the total heat capacity of the calorimetric system was 12.60 grams instead of 12.24 grams as given before, on account of the use of other rubber stoppers weighing 4.05 grams (instead of 3.30 grams).   Because of the smaller specific heat of hydrochloric acid as well as its greater density, about 466.5 grams of this acid were used in the calorimeter, instead of 450.2 grams as in the case of water.   A preliminary series of eight experiments gave an average rise of temperature under these conditions (the average final temperature being 20.34) of 4.231°.   This corresponds to a specific heat possessed by the hydrochloric acid of 0.9635, with a probable error (computed according to the method of least squares) of 0.0002.   The individual results need not be given, as they were only approximate, but none deviated more than 0.1 percent from the mean.   A single experiment taken at random from the much more satisfactory final series will be recorded in detail before this series is summarized.

DATA OF A SPECIMEN DETERMINATION OF THE SPECIFIC HEAT OF $HCl.100H_2O$.

Series 2B, No. 1.   Jan. 17, 1910.

Temperature Data.

Initial thermometer reading	=	16.120°	
Total Calibration correction	= −	0.038	
Initial temperature (corrected) (T_1)			16.082°
Final temperature reading	=	20.344°	
Total Calibration correction	= −	0.030°	
Final temperature (corrected) (T_2)			20.314°
(T_2-T_1)		=	4.232°
Stem exposure corr.		= +	0.001°
Temperature interval (T_2-T_1) corrected		=	4.233°

Heat evolved by neutralization of acid: —

Weight of acid	=	114.87 gms.
Q for 100.00 grams at 20.31°	= 2170.7	cals.[11]
Q for 114.87 grams at 20.31°	= 2493.4	"

11 This value is calculated from the preceding Table II.

Heat capacity data. (in terms of water equivalent)

Heat capacity of acid   = x
Calorimeter system   =   12.60 gms.
NaOH   =   17.83   "
H_2SO_4 (114.87 gms.)   = 109.13   "

Total heat capacity =   = $x + 139.56$

Then heat evolved equals $(x + 139.56) \times 4.233 = 2493.4$ cal.

$$\text{Hence, } x = 449.47 \frac{\text{calories}}{\text{degrees}}$$

But the weight of HCl.100 H_2O actually taken in the calorimeter was 466.54 grams. Hence its specific heat

$$= \frac{\text{heat capacity}}{\text{heat capacity of equal weight } H_2O} = \frac{449.47}{466.54} = 0.9634$$

Immediately below is tabulated a series of determinations of this kind, giving all the necessary data.

TABLE IV.

Series Concerning the Specific Heat of HCl. 100 H_2O.

No.	Sample HCl.	HCl·100 H_2O.	H_2SO_4.	T_2.	$T_2 - T_1$.	Specific HCl·100 H_2O.	
				Series 2A.			
		gms.					
1	A	466.52	114.86	20.00	4.237	0.9634	
2	A	466.52	144.87	19.99	4.236	0.9637	Average.
3	A	466.51	114.86	20.21	4.236	0.9628	0.9633
				Series 2B.			
1	B	466.54	114.87	20.31	4.233	0.9634	
2	B	466.55	114.86	19.75	4.237	0.9641	
3	B	466.50	114.86	20.08	4.239	0.9626	Average.
4	B	466.51	114.86	20.50	4.230	0.9636	0.9634
Total av'ge		466.52	114.863	20.12	4.235	0.9634	0.9634

The mean value, then, for the specific heat of $HCl.100H_2O$ over the range between $15.9°$ and $20.1°$ is 0.9634 compared with water over the same range of temperature. This is equal to the results found in the preliminary series, within the range of the probable error (0.0001). It will be noted that the maximum difference from the mean is considerably less than 0.1 percent. The probable error of the seven determinations is only about 1 in the fourth decimal place. These determinations are typical of the experiments made with the other solutions. Because of the great similarity of the experiments to one another, it will not be necessary to record every experiment, but the average values similar to the total averages given on the last line of the table above will be given for each of the essential data, together with the number of experiments.

In the course of the experiments first performed, namely, all those on hydrochloric acid and sodium hydroxide, the original preparation of sulphuric acid was exhausted. This solution (designated A) contained, as has been already stated, 6.275 percent of sulphuric acid. For the remaining experiments it was necessary to prepare a new solution (designated B below) which was found to contain 6.283 percent of acid.[12]   In order to make assurance doubly sure, this new solution was used in ten experiments with pure water in the calorimeter which are recorded at the foot of the table below. The slightly greater strength of the acid caused the average rise of temperature to be slightly greater in this last series than in the first. At $20.19°$ the original acid would have caused a rise of $4.229°$, and with this new acid, 0.13 percent more concentrated, the rise was $4.234°$ — an exact proportionality. No more satisfactory evidence of the consistency of the work could have been desired.

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[12] In this connection a somewhat interesting demonstration of the accuracy of the method was obtained. The sulphuric acid was originally analyzed by titration with a sodium hydroxide solution which had been carefully standardized but which had stood for some months in a paraffin-lined bottle. The mean of the analyses thus conducted, gave the strength as 6.272 percent. When the heat evolved during the neutralization of $\frac{1}{2}$ molecule of acid was determined and compared with that shown by the previous lot of acid, the observed and calculated results showed a serious discrepancy. The strength of the new acid was calculated *from the thermal data* and found to be 6.282 percent. Investigation of the bottle containing the standard alkali showed a break in the paraffin lining which had permitted contact between the glass and the solution; hence the alkali had become slightly more alkaline; a fresh alkali solution was prepared and carefully standardized and by its use the acid was again analyzed. The result of these analyses is the figure given above, namely, 6.283 percent or within 0.02 percent of that calculation from the thermal data. It is clear, therefore, that the calorimetric process had been so effectively arranged as to constitute a very accurate process of quantitative acidimetric analysis.

Of course, in each case where acid *B* was used, the higher value must be used in the computation, whereas in each case where acid *A* was used, the lower value is the proper one.

In the following table each series of experiments used the average quantity 114.863 grams of sulphuric acid per experiment — at least the deviation from this average amount was smaller than the probable experimental error, so that the amount may be taken as a constant. In none of the individual experiments except in the first series with water (Table II), did the amount of acid exceed 114.87 grams or sink below 114.85 grams. The averages for the several series were much closer to 114.863 than this. The heat capacity of the solid apparatus also was constant, being always 12.60 grams except in the first four experiments with water already tabulated; and a constant amount of caustic alkali was used as always. The other quantities found in the experiments are given in the following table, the figures there being (as has been said) total averages similar to those given at the foot of the table just above. Because of the great similarity of the experiments, it does not seem worth while to give each one in detail. Anyone can calculate for himself the average results for the specific heats from the data given below. The only essential figures not immediately indicated by the table are the deviations among the individual experiments, but these are sufficiently shown by the "probable errors" given in the last column, calculated according to the theory of least squares. From this it will be seen that two of the series were somewhat less concordant than that given above, but most of them were fully as good as the sample series, or indeed even better. In another respect, also, perhaps, this table of averages does not quite do justice to the work:— it does not give a vivid representation of the very large expenditure of labor, extending over many months, which was needed to obtain the numerous results so concisely tabulated.

The main object in determining these specific heats was to provide a basis for computing the heats of neutralization of the various substances in question, but the values are nevertheless not without interest in themselves.

The significance of results of this sort are of course most easily perceived when the results are computed in terms of gram-molecules, and after this has been done, two sets of comparisons are possible: — in the first place, the effect of dilution upon the molecular heat of a given substance, and in the next place the effect of varying the ions concerned.

TABLE V.

DATA AND RESULTS OF DETERMINATION OF SPECIFIC HEATS.

	No. of Exp.	Sample of H_2SO_4.	Average Weight of Solution.	Average Final Temp.	Av'ge Rise of Temp. °C.	Sp. Heat (Range about 16-20.2°.)	Probable Error.
H_2O at 19.77°	513	A	450.18	19.77°	4.234	Standard	
H_2O at 20.39°	414	A	450.18	20.39	4.227	Ch'k exp.	
H_2O at 20.72°	315	A	450.18	20.72°	4.225	Standard	
HCl 200H_2O	8	A	458.99	20.24	4.226	0.9814	±0.0002
HCl 100H_2O	7	A	466.52	20.12	4.235	0.9634	±0.0001
HBr 100H_2O	4	B	471.18	20.29	4.276	0.9433	±0.0000
HI 100H_2O	6	B	480.20	20.41	4.2885	0.9213	±0.0001
HNO_3 100H_2O	7	B	467.45	20.31	4.249	0.9584	±0.0002
$HClO_4$ 100H_2O	4	B	471.17	20.34	4.283	0.9466	±0.0001
KOH 100H_2O	4	B	471.18	20.04	4.232	0.9568	±0.0001
NaOH 100H_2O	6	A	465.13	20.29	4.233	0.9664	±0.0001
NaOH 200H_2O	7	A	457.97	20.08	4.231	0.9827	±0.0001
LiOH 100H_2O	5	B	461.19	20.34	4.2154	0.9813	±0.0001
H_2O at 20.19°	10	B	450.18	20.19	4.234	Standard	

Let us consider first the effect of diluting the hydrochloric acid. The solution HCl.100 H_2O weighs per gram molecule of hydrochloric acid $36.46 + 1801.5$ grams. With a specific heat 0.9634 this gives a molecular heat 1770.6. When 100 gram molecules of water have been added to this solution, it then has a total molecular weight 3639.5 and a molecular heat capacity of 3571.8 calculated from its specific heat 0.9814. The difference between the total molecular heat capacities of these two solutions is 1801.2 or almost the same as

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13 See Table II.
14 See Table III.
15 See Table II.

the heat capacity 1801.5 of the added water. The slight decrease is no larger than the possible experimental error; but it is probable that the dilute solution really does suffer a small diminution of about this order.

Carrying out the same calculation for sodium hydroxide we find the molecular heat capacity for NaOH.100 H_2O, 1780, and that for NaOH.200 H_2O to be 3580. The difference here again is slightly less than the heat capacity of the added water, being 1800, instead of 1801.5 — a difference of almost 0.1 percent.

Evidently solutions of strong bases and acids containing as much as 100 molecules of water (about half normal in equivalent concentration) are already so dilute that most of the added water is unaffected,— or at least, such small changes as the water suffers must be balanced by contrary effects. Thus the specific heat of any more dilute solution may be calculated with considerable precision from the data contained in this paper.

Turning now to the comparison of the different substances, all in solutions containing 100 molecules of water for each molecule of dissolved substance, we find other interesting and significant relations. The following table presents the molecular heats of all the substances for comparison:—

TABLE XIV.

The Molecular Heats of the Acid and Alkali Solutions of the Type MX. 100 H_2O

Solution.	Molecular Weight.	Specific Heat.	Molecular Heat.
HCl	1801.5 + 36.46	0.9634	1771
HBr	" + 80.92	.9433	1776
HI	" + 128.00	.9213	1778
HNO³	" + 63.02	.9584	1787
HClO⁴	" + 100.46	.9466	1801
LiOH	" + 23.95	.9813	1791
NaOH	" + 40.00	.9664	1780
KOH	" + 56.10	.9568	1777

From this table it is clear that the molecular heat increases with the molecular weight in the case of the halogen acids. The further increase in the case of nitric and perchloric acid is only to be expected from the increasing size and complexity of these molecules. On the other hand it is noticeable that in the case of the alkalies the molecular heats diminish as the atomic weight of the metal increases.

Of course many circumstances lie at the basis of these phenomena; the degree of ionization, the degree of hydration of both the ions and of the undissociated substance; and indeed all those other as yet undetermined factors which together produce the specific volumes and all the other properties of solutions come into play here also. Whatever may be the ultimate interpretation of these matters, it is clear that the data just given must receive consideration in the final estimate of the situation.

Summary.

In this communication an improved apparatus for the determination of the specific heats of solutions or other liquids has been described. The method depends upon the liberation of definite quantities of heat by the neutralization of definite quantities of pure sulphuric acid.

The apparatus is capable of giving results of great accuracy. The individual deviations are such that with five or six experiments the "probable error" of the average specific heat is usually less than 0.0001. Because of this high degree of accuracy, it is evident that the mercury thermometers used are an adequate means of measuring temperature for this purpose.

With this apparatus the specific heats of dilute solutions of hydrochloric, hydrobromic, hydriodic, nitric, and perchloric acids, as well as of lithium, sodium, and potassium hydroxides have been determined.

From these results the molecular heats of the solutions have been calculated, and relations between them pointed out. It is shown that the molecular heats vary in a systematic manner.